

BaMn^{II}₂Mn^{III}(PO₄)₃

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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{P}-\text{O}) = 0.002$ Å;
R factor = 0.020; wR factor = 0.055; data-to-parameter ratio = 15.3.

The title compound, barium trimanganese tris(orthophosphate), was synthesized hydrothermally. Its structure is isotopic with the lead and strontium analogues $AMn^{II}_2Mn^{III}(\text{PO}_4)_3$ ($A = \text{Pb, Sr}$). Except for two O atoms on general positions, all atoms are located on special positions. The Ba and one P atom exhibit $mm2$ symmetry, the Mn^{II} atom $2/m$ symmetry, the Mn^{III} atom and the other P atom $.2.$ symmetry and two O atoms are located on mirror planes. The crystal structure contains two types of chains running parallel to [010]. One chain is linear and is composed of alternating Mn^{III}O₆ octahedra and PO₄ tetrahedra sharing vertices; the other chain has a zigzag arrangement and is built up from two edge-sharing Mn^{II}O₆ octahedra connected to PO₄ tetrahedra by edges and vertices. The two types of chains are linked through PO₄ tetrahedra into an open three-dimensional framework which contains channels parallel to [100] and [010] in which the Ba^{II} ions are located. The alkaline earth cation is surrounded by eight O atoms in the form of a slightly distorted bicapped trigonal prism.

Related literature

For the isotopic lead and strontium analogues, see: Alhakmi *et al.* (2013a) and (2013b), respectively. For related structures, see: Adam *et al.* (2009); Assani *et al.* (2011a,b). For bond-valence analysis, see: Brown & Altermatt (1985). For the by-product phase, see: Moore & Araki (1973).

Experimental*Crystal data*

$\text{BaMn}_3(\text{PO}_4)_3$
 $M_r = 587.07$
Orthorhombic, $Imma$
 $a = 10.3038 (7)$ Å
 $b = 14.0163 (11)$ Å
 $c = 6.7126 (4)$ Å

$V = 969.44 (12)$ Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 8.39$ mm⁻¹
 $T = 296$ K
 $0.29 \times 0.17 \times 0.13$ mm

Data collection

Bruker X8 APEX diffractometer
Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)
 $T_{\min} = 0.164$, $T_{\max} = 0.376$

3968 measured reflections
811 independent reflections
732 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.055$
 $S = 1.09$
53 parameters
 $\Delta\rho_{\max} = 1.86$ e Å⁻³
 $\Delta\rho_{\min} = -0.78$ e Å⁻³

811 reflections

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2767).

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supplementary materials

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BaMn^{II}₂Mn^{III}(PO₄)₃

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1. Comment

Investigating functional compounds by means of the hydrothermal process, particularly phosphates, we have succeeded to synthesize and structurally characterize new mixed-cation orthophosphates with open frameworks, e.g. the isotopic pair $Ag_2M_3(HPO_4)(PO_4)_2$ ($M = Co, Ni$) (Assani *et al.*, 2011*a,b*) that is closely related to the alluaudite structure. Others investigated phosphates include compounds crystallizing in the $AMn^{II}2Mn^{III}(PO_4)_3$ ($A = Pb, Sr$) structure type (Alhakmi *et al.* (2013*a,b*) with rarely observed mixed-valent Mn^{II/III} cations (Adam *et al.*, 2009). The present article reports on synthesis and crystal structure of the isotopic barium analogue, $BaMn^{II}2Mn^{III}(PO_4)_3$.

All atoms of this structure are in special positions, except two oxygen atoms (O3, O4) in general position of space group *Imma*. The connection of the metal-oxygen polyhedra, *viz.* BaO₈ polyhedra, MnO₆ octahedra and PO₄ tetrahedra is shown in Fig. 1. The framework of the crystal structure consists of two isolated PO₄ tetrahedra linked to MnO₆ octahedra, building two types of chains running along [010]. The first chain is formed by alternating Mn^{III}O₆ octahedra and PO₄ tetrahedra sharing vertices. The second chain is built up from two edge-sharing Mn^{II}O₆ octahedra leading to the formation of Mn^{II}₂O₁₀ dimers that are connected to two PO₄ tetrahedra by a common edge. These two types of chains are linked together by common vertices of PO₄ tetrahedra to form an open three-dimensional framework that delimits two types of tunnels parallel to [100] and [010] where the Ba^{II} ions are located (Fig. 2). The coordination sphere of the Ba^{II} ion is that of a bicapped trigonal prism.

Bond valence sum calculation (Brown & Altermatt, 1985) of $BaMn^{II}2Mn^{III}(PO_4)_3$ resulted in expected values (in valence units) for the ions Ba1^{II} (2.26), Mn1^{III} (3.01), Mn2^{II} (2.09), P1^V (4.99), and P2^V (4.87). The three-dimensional framework of $BaMn^{II}2Mn^{III}(PO_4)_3$ and its isotopic $AMn^{II}2Mn^{III}(PO_4)_3$ ($A = Pb, Sr$) analogues, resemble that of the $Ag_2M_3(HPO_4)(PO_4)_2$ type with $M = Ni$ or Co , whereby the two Ag⁺ cations in the channels are replaced by Ba^{II}, Pb^{II} or Sr^{II}.

2. Experimental

The hydrothermal treatment of a reaction mixture of barium, manganese and phosphate precursors in a proportion corresponding to the molar ratio Ba: Mn: P = 1: 3: 3 has allowed to isolate brown block-shaped crystals corresponding to the title compound as well as a parallelepipedic colourless crystals which were identified to be the known manganese phosphate Mn₅(HPO₄)₂(PO₄)₂·4H₂O (Moore & Araki, 1973). The hydrothermal reaction was conducted in a 23 ml Teflon-lined autoclave, filled to 50% with distilled water and under autogeneous pressure at 463 K for five days.

3. Refinement

The highest peak and the deepest hole in the final Fourier map are at 0.82 Å and 1.00 Å away from Ba1.

Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

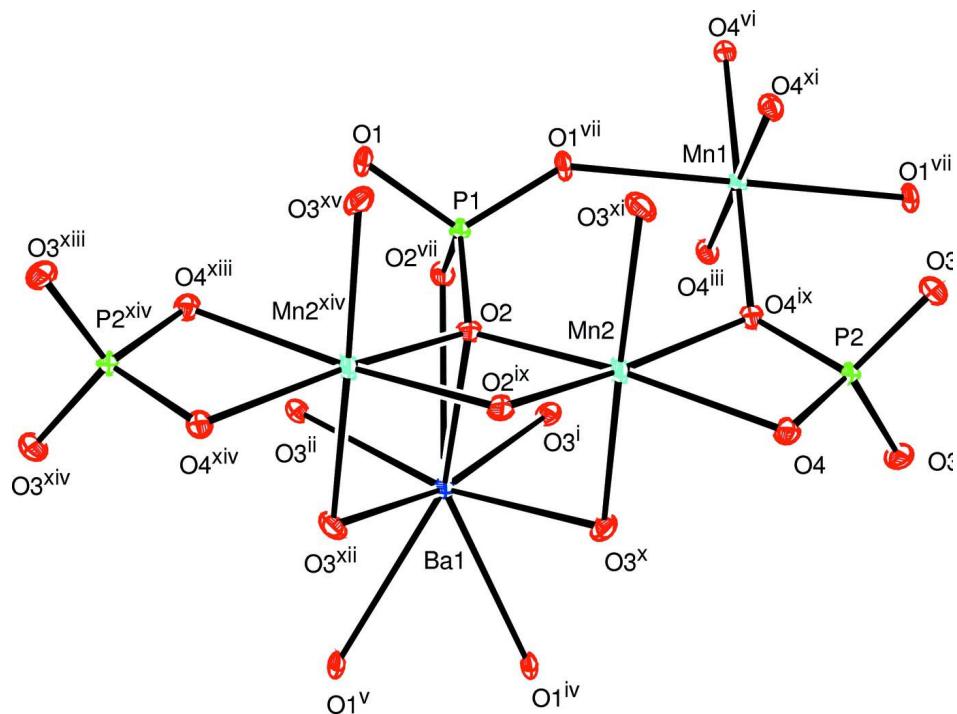
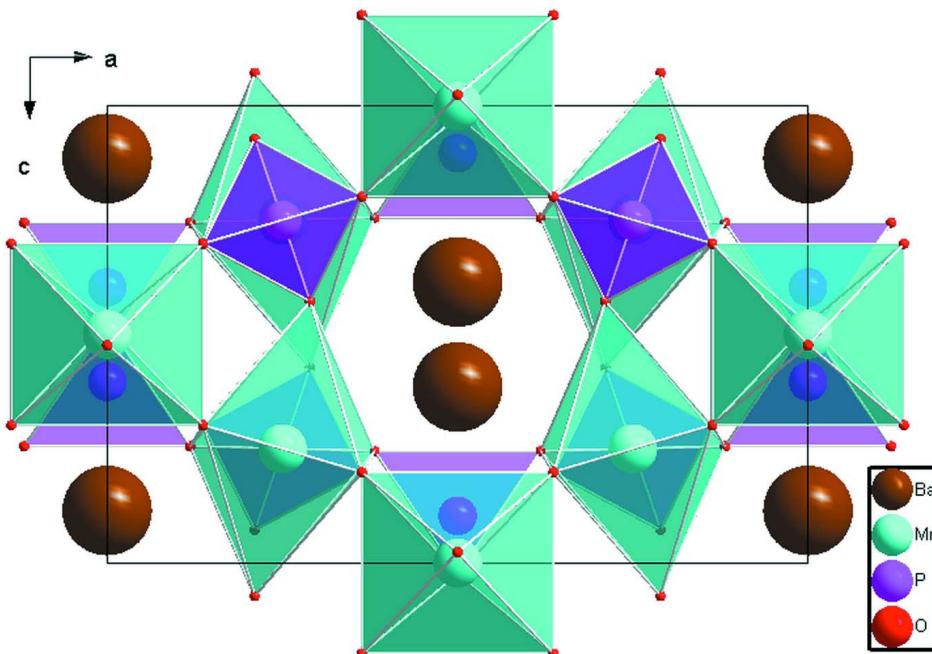


Figure 1

The main building units of the crystal structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x, -y + 1, -z$; (ii) $-x, y - 1/2, -z$; (iii) $x, y - 1/2, -z$; (iv) $-x, -y + 1, -z$; (v) $x, y, z - 1$; (vi) $-x, -y + 1/2, z - 1$; (vii) $-x, -y + 1/2, z$; (viii) $-x + 1/2, y - 1/2, z + 1/2$; (ix) $x - 1/2, -y + 1/2, -z + 1/2$; (x) $-x + 1/2, -y + 1/2, -z + 1/2$; (xi) $x - 1/2, y - 1/2, z + 1/2$; (xii) $-x, -y, -z + 1$; (xiii) $-x + 1/2, -y + 1, z + 1/2$; (xiv) $-x + 1/2, y, -z + 1/2$.]

**Figure 2**

Polyhedral representation of $\text{BaMn}_3(\text{PO}_4)_3$ with channels running parallel to [010].

Barium trimanganese tris(orthophosphate)

Crystal data

$\text{BaMn}_3(\text{PO}_4)_3$

$M_r = 587.07$

Orthorhombic, $Imma$

Hall symbol: -I 2b 2

$a = 10.3038 (7) \text{ \AA}$

$b = 14.0163 (11) \text{ \AA}$

$c = 6.7126 (4) \text{ \AA}$

$V = 969.44 (12) \text{ \AA}^3$

$Z = 4$

$F(000) = 1088$

$D_x = 4.022 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 811 reflections

$\theta = 3.4\text{--}30.5^\circ$

$\mu = 8.39 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Block, brown

$0.29 \times 0.17 \times 0.13 \text{ mm}$

Data collection

Bruker X8 APEX

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2009)

$T_{\min} = 0.164$, $T_{\max} = 0.376$

3968 measured reflections

811 independent reflections

732 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 30.5^\circ$, $\theta_{\min} = 3.4^\circ$

$h = -14 \rightarrow 13$

$k = -19 \rightarrow 20$

$l = -9 \rightarrow 7$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.020$

$wR(F^2) = 0.055$

$S = 1.09$

811 reflections

53 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
 $w = 1/[\sigma^2(F_o^2) + (0.0353P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.86 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.78 \text{ e \AA}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against all reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on all data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^* / U_{\text{eq}}$
Ba1	0.0000	0.2500	-0.11499 (4)	0.01125 (10)
Mn1	0.0000	0.5000	0.5000	0.00794 (15)
Mn2	0.2500	0.36758 (4)	0.2500	0.01092 (13)
P1	0.0000	0.2500	0.39677 (16)	0.0078 (2)
P2	0.2500	0.57094 (6)	0.2500	0.00851 (17)
O1	0.0000	0.15998 (16)	0.5237 (4)	0.0115 (5)
O2	0.1185 (2)	0.2500	0.2553 (3)	0.0107 (4)
O3	0.21046 (19)	0.63040 (12)	0.0721 (3)	0.0133 (3)
O4	0.36337 (16)	0.49927 (12)	0.1983 (2)	0.0103 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.01480 (16)	0.01187 (15)	0.00707 (14)	0.000	0.000	0.000
Mn1	0.0102 (3)	0.0081 (3)	0.0056 (3)	0.000	0.000	-0.0001 (2)
Mn2	0.0154 (3)	0.0063 (2)	0.0110 (2)	0.000	-0.00074 (18)	0.000
P1	0.0104 (5)	0.0065 (5)	0.0066 (5)	0.000	0.000	0.000
P2	0.0121 (4)	0.0064 (4)	0.0071 (3)	0.000	0.0010 (3)	0.000
O1	0.0166 (12)	0.0049 (9)	0.0129 (11)	0.000	0.000	0.0014 (8)
O2	0.0121 (11)	0.0103 (11)	0.0098 (10)	0.000	0.0035 (8)	0.000
O3	0.0183 (8)	0.0114 (8)	0.0100 (7)	0.0027 (6)	0.0006 (7)	0.0033 (6)
O4	0.0123 (8)	0.0087 (7)	0.0100 (7)	0.0014 (6)	0.0016 (6)	0.0009 (5)

Geometric parameters (\AA , $^\circ$)

Ba1—O1 ⁱ	2.734 (2)	Mn2—O2	2.1337 (16)
Ba1—O1 ⁱⁱ	2.734 (2)	Mn2—O2 ^{xii}	2.1337 (16)
Ba1—O3 ⁱⁱⁱ	2.7560 (18)	Mn2—O3 ⁱⁱⁱ	2.2006 (17)
Ba1—O3 ^{iv}	2.7560 (18)	Mn2—O3 ^{ix}	2.2006 (17)
Ba1—O3 ^v	2.7560 (18)	Mn2—O4	2.2117 (17)
Ba1—O3 ^{vi}	2.7560 (18)	Mn2—O4 ^x	2.2117 (17)
Ba1—O2	2.769 (2)	P1—O1	1.523 (2)
Ba1—O2 ^{vii}	2.769 (2)	P1—O1 ^{vii}	1.523 (2)

Mn1—O4 ^{viii}	1.9377 (17)	P1—O2 ^{vii}	1.547 (2)
Mn1—O4 ^{ix}	1.9377 (17)	P1—O2	1.547 (2)
Mn1—O4 ^x	1.9377 (17)	P2—O3 ^x	1.5119 (17)
Mn1—O4 ^{xi}	1.9377 (17)	P2—O3	1.5119 (17)
Mn1—O1 ^{vii}	2.248 (2)	P2—O4 ^x	1.5792 (17)
Mn1—O1 ^{xii}	2.248 (2)	P2—O4	1.5792 (17)
O1 ⁱ —Ba1—O1 ⁱⁱ	54.97 (9)	O4 ^{ix} —Mn1—O1 ^{vii}	87.51 (6)
O1 ⁱ —Ba1—O3 ⁱⁱⁱ	111.92 (5)	O4 ^x —Mn1—O1 ^{vii}	92.49 (6)
O1 ⁱⁱ —Ba1—O3 ⁱⁱⁱ	79.16 (5)	O4 ^{xi} —Mn1—O1 ^{vii}	87.51 (6)
O1 ⁱ —Ba1—O3 ^{iv}	79.16 (5)	O4 ^{viii} —Mn1—O1 ^{xii}	87.51 (6)
O1 ⁱⁱ —Ba1—O3 ^{iv}	111.92 (5)	O4 ^{ix} —Mn1—O1 ^{xii}	92.49 (6)
O3 ⁱⁱⁱ —Ba1—O3 ^{iv}	168.02 (7)	O4 ^x —Mn1—O1 ^{xii}	87.51 (6)
O1 ⁱ —Ba1—O3 ^v	79.16 (5)	O4 ^{xi} —Mn1—O1 ^{xii}	92.49 (6)
O1 ⁱⁱ —Ba1—O3 ^v	111.92 (5)	O1 ^{vii} —Mn1—O1 ^{xii}	180.0
O3 ⁱⁱⁱ —Ba1—O3 ^v	74.93 (8)	O2—Mn2—O2 ^{xiii}	78.86 (10)
O3 ^{iv} —Ba1—O3 ^v	103.78 (8)	O2—Mn2—O3 ⁱⁱⁱ	84.77 (8)
O1 ⁱ —Ba1—O3 ^{vi}	111.92 (5)	O2 ^{xiii} —Mn2—O3 ⁱⁱⁱ	96.38 (8)
O1 ⁱⁱ —Ba1—O3 ^{vi}	79.16 (5)	O2—Mn2—O3 ^{ix}	96.38 (8)
O3 ⁱⁱⁱ —Ba1—O3 ^{vi}	103.78 (8)	O2 ^{xiii} —Mn2—O3 ^{ix}	84.77 (8)
O3 ^{iv} —Ba1—O3 ^{vi}	74.93 (8)	O3 ⁱⁱⁱ —Mn2—O3 ^{ix}	178.52 (9)
O3 ^v —Ba1—O3 ^{vi}	168.02 (7)	O2—Mn2—O4	169.28 (7)
O1 ⁱ —Ba1—O2	142.77 (4)	O2 ^{xiii} —Mn2—O4	107.86 (7)
O1 ⁱⁱ —Ba1—O2	142.77 (4)	O3 ⁱⁱⁱ —Mn2—O4	86.16 (6)
O3 ⁱⁱⁱ —Ba1—O2	63.86 (5)	O3 ^{ix} —Mn2—O4	92.61 (7)
O3 ^{iv} —Ba1—O2	104.67 (5)	O2—Mn2—O4 ^x	107.86 (7)
O3 ^v —Ba1—O2	63.86 (5)	O2 ^{xiii} —Mn2—O4 ^x	169.28 (7)
O3 ^{vi} —Ba1—O2	104.67 (5)	O3 ⁱⁱⁱ —Mn2—O4 ^x	92.61 (7)
O1 ⁱ —Ba1—O2 ^{vii}	142.77 (4)	O3 ^{ix} —Mn2—O4 ^x	86.16 (6)
O1 ⁱⁱ —Ba1—O2 ^{vii}	142.77 (4)	O4—Mn2—O4 ^x	66.86 (9)
O3 ⁱⁱⁱ —Ba1—O2 ^{vii}	104.67 (5)	O1—P1—O1 ^{vii}	111.94 (19)
O3 ^{iv} —Ba1—O2 ^{vii}	63.86 (5)	O1—P1—O2 ^{vii}	110.09 (7)
O3 ^v —Ba1—O2 ^{vii}	104.67 (5)	O1 ^{vii} —P1—O2 ^{vii}	110.09 (7)
O3 ^{vi} —Ba1—O2 ^{vii}	63.86 (5)	O1—P1—O2	110.09 (7)
O2—Ba1—O2 ^{vii}	52.33 (10)	O1 ^{vii} —P1—O2	110.09 (7)
O4 ^{viii} —Mn1—O4 ^{ix}	180.0	O2 ^{vii} —P1—O2	104.27 (19)
O4 ^{viii} —Mn1—O4 ^x	93.19 (10)	O3 ^x —P2—O3	113.10 (14)
O4 ^{ix} —Mn1—O4 ^x	86.81 (10)	O3 ^x —P2—O4 ^x	112.12 (9)
O4 ^{viii} —Mn1—O4 ^{xi}	86.81 (10)	O3—P2—O4 ^x	108.95 (10)
O4 ^{ix} —Mn1—O4 ^{xi}	93.19 (10)	O3 ^x —P2—O4	108.95 (10)
O4 ^x —Mn1—O4 ^{xi}	180.0	O3—P2—O4	112.12 (9)
O4 ^{viii} —Mn1—O1 ^{vii}	92.49 (6)	O4 ^x —P2—O4	100.99 (13)

Symmetry codes: (i) $x, y, z-1$; (ii) $-x, -y+1/2, z-1$; (iii) $x, -y+1, -z$; (iv) $-x, y-1/2, -z$; (v) $x, y-1/2, -z$; (vi) $-x, -y+1, -z$; (vii) $-x, -y+1/2, z$; (viii) $x-1/2, y, -z+1/2$; (ix) $-x+1/2, -y+1, z+1/2$; (x) $-x+1/2, y, -z+1/2$; (xi) $x-1/2, -y+1, z+1/2$; (xii) $x, y+1/2, -z+1$; (xiii) $-x+1/2, -y+1/2, -z+1/2$.